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LIQUID AND FROZEN EGG

V. VISCOSITY, BAKING QUALITY, AND OTHER MEASUREMENTS ON FROZEN EGG PRODUCTS[1]

BY JESSE A. PEARCE[2] AND C. G. LAVERS[3]

Abstract

Freezing irreversibly increased the viscosity of yolk and whole egg, but did not affect the white. Vigorous mechanical treatment before freezing reduced the viscosity of defrosted yolk, white, and whole egg. The viscosity of defrosted yolk and whole egg increased with increase in freezing or thawing time. Mechanical pretreatment or differences in freezing time did not affect the baking quality of defrosted egg products. Freezing reduced the baking quality of yolk and whole egg, but the baking quality improved after storage for about three months at − 10° and 0° F., and then decreased. A thawing time of four hours resulted in yolk or whole egg of better baking quality than thawing times of 0.03, 24, or 48 hr. There was no relation between viscosity and the baking quality of these egg products. The addition of 2% sodium chloride was equivalent to the addition of 8% sucrose in preserving the foaming quality of frozen yolk.

Introduction

Previous papers in this series have been concerned primarily with the development of tests for measuring eating quality and for determining the solids content of frozen egg. Since frozen egg is used chiefly by the baking trade, it was believed desirable to assess the effects of prefreezing treatment, freezing time, storage time, and thawing time on the baking quality of defrosted egg products. This paper describes the effect of all these factors on baking quality, as assessed by measurements of baking volume or foaming volume (7); and the effect of some of them on other measures, such as viscosity (9), fluorescence value (6), and amino nitrogen (11).

Materials and Methods

Fresh Grade *A* large eggs were used to prepare the experimental materials, which, unless otherwise stated, were mixed for five minutes in a "Mixmaster" at No. 10 speed, strained through cheese cloth to remove particles of shell and chalaza, poured into Reynold's metal A-10 bags with a capacity of about

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[2] *Biochemist, Food Investigations.*
[3] *Formerly Chemical Engineer, Food Investigations; present address, Research Department, Maple Leaf Milling Co., Toronto.*

one liter (3 by 4 by 5 in.), and frozen in about 10 hr. Freezing was considered complete when a thermocouple in the center of the block of egg reached 20° F. at which point approximately 6% of the water remains unfrozen (8). The time for the liquid to pass from about 45° to 20° F. was recorded as the freezing time.

Defrosting was done in about 15 hr., unless otherwise stated. Defrosting time was defined as the time for the liquid to pass from a temperature of 0° F. to about 35° to 40° F. After defrosting and before testing, the liquid was again mixed at a temperature of 50° F. in a "Mixmaster" for one minute at No. 1 speed. White and whole egg usually became reasonably homogeneous after this mixing period, but as mixing did not make the more viscous samples of yolk homogeneous, their viscosity was tested in the heterogeneous state.

Many of the tests were those used in previous studies in this series (4), and included measurements of pH, reducing sugar, viable bacterial count, volume measurements on test sponge cakes, and foaming volume measurements. Baking and foaming volume measurements were made on defrosted white mixed with freshly separated yolk and on defrosted yolk mixed with freshly separated white. These mixtures were equivalent in composition to freshly broken whole egg. For these baking quality tests, the most viscous yolk could be mixed with egg white, but it was more difficult to use than yolk of low viscosity.

Fluorescence was measured on a serum extracted from whole egg (6), and amino nitrogen was determined in whole egg and in yolk by Van Slyke's method (11). Viscosity was measured on defrosted egg liquids at 50° F. with a Gardner–Parks mobilometer (9), which consists of a cylinder to contain the liquid under study, and a piston that is allowed to fall a measured distance through the liquid. The pistonhead can be changed to provide more or less resistance and the weight on the piston can be varied. The 51-hole disk (pistonhead) was used with a total weight of 100 gm. including the piston for defrosted white, or whole egg, and with a total weight of 1600 gm. for defrosted yolk. The time in seconds for the piston to fall 20 cm. was taken as a measure of viscosity.

Effect of Prefreezing Treatment on Quality

Mechanical treatment of whole egg before freezing was believed to retard the gelation that occurs during frozen storage (9). This phase of the study was designed to examine the effect of mechanical treatment of whole egg, yolk, and white on viscosity, baking quality, and pH of the stored, frozen product. Strained liquid was treated in four ways: no further treatment, 15 min. additional mixing, dispersion in a laboratory hand homogenizer, and dispersion in a colloid mill. All mixing and dispersing was done in a manner that minimized the introduction of air and the resulting foam. The products were stored at −10° F.

The various mechanical treatments did not affect the baking volume, foaming volume, or pH of whole egg, yolk, or white, whether measured before freezing, after freezing or after frozen storage.

Table I shows that increasing the severity of the mechanical treatment reduced the mobilometer readings, i.e., the viscosity, of unfrozen and defrosted whole egg, yolk, and white. Average readings are given in the table because none of the materials showed any change in viscosity during storage for three

TABLE I

EFFECT OF MECHANICAL TREATMENT ON THE VISCOSITY OF UNFROZEN AND DEFROSTED EGG PRODUCTS

Treatment	Mobilometer reading, sec.	
	Before freezing	After freezing*
Whole egg		
Mixed		
Mix. 5 min.	3.2	178
Mix 20 min.	2.4	151
Dispersed		
Mix 5 min. + homogenizer	1.5	10
Mix 5 min. + colloid mill	1.3	10
Yolk (1600 gm. weight on piston when used on defrosted yolk)		
Mixed		
Mix 5 min.	27	455
Mix 20 min.	26	315
Dispersed		
Mix 5 min. + homogenizer	19	236
Mix 5 min. + colloid mill	18	129
White		
Mixed		
Mix 5 min.	6.5	4.0
Mix 20 min.	2.9	2.6
Dispersed		
Mix 5 min. + homogenizer	1.3	1.3
Mix 5 min. + colloid mill	1.1	1.1

**Average after storage for 0, 1, 2, and 3 months at − 10° F.*

months at −10° F. Freezing did not change the viscosity of egg white, regardless of the treatment. Freezing increased the viscosity of the mixed (Mixmaster only) whole egg about 60 times but only increased the viscosity of the dispersed (colloid mill or homogenizer) whole egg by about eight times. Freezing caused so great an increase in the viscosity of yolk that the weight on the piston had to be increased from 100 to 1600 gm., which interferes with comparisons of the data. Nevertheless there is evidence that dispersed yolk changes less in viscosity during freezing than the mixed yolk.

Effect of Freezing Time on Quality

The liquid was frozen at different temperatures and with different thicknesses of insulation around the Reynold's metal containers, to provide different freezing rates. The bacterial count in the initial, laboratory-prepared material was only about 50 per ml. A count of the same order was observed in products frozen in less than 12 hr., but the count increased to 300 per ml. in product frozen in about 24 hr. and to 1000 per ml. in product frozen in 100 hr. High bacterial counts are usually observed in the cores of commercially prepared cans of egg that have been frozen too slowly. However, after a period of frozen storage, there is usually a marked decrease in the bacterial count (2, 12).

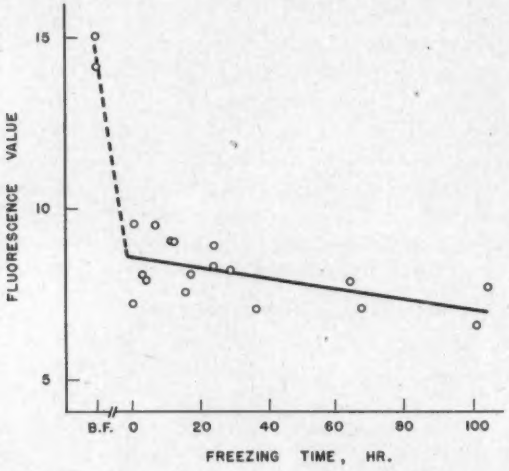

FIG. 1. *Effect of time of freezing on the fluorescence value of a serum extracted from whole egg.*

A visual examination of the effect of freezing time on color and structure showed that material frozen in 10 min. was light yellow in color. As the freezing time was increased, the color of the product deepened, and at a freezing time of 110 hr. became a dark orange. The frozen product had a laminar structure. If frozen in 10 min., the flakes were alternately opaque and transparent and about 0.001 in. thick. If frozen in 25 hr. the flakes were about 0.05 in. thick, while material frozen in 60 and 100 hr. had a granular structure to a depth of about 2 in., but the center had a laminar structure in which the transparent flakes were about 0.1 in. thick.

Freezing and the time of freezing had no effect on either the reducing sugar or the amino nitrogen content of eggs. The reducing sugar content of whole egg remained at 0.38 mgm. per 100 ml. of egg, regardless of the freezing time. The amino nitrogen content of 5-ml. samples of whole egg and of yolk was 6.90 and 9.66 mgm. respectively, whether frozen or unfrozen.

Fig. 1 shows that freezing appreciably reduced the fluorescence of a serum extracted from whole egg. Increasing the freezing time from about 10 min. to 100 hr. reduced the fluorescence of this extract still further. It is unlikely that this is due to factors other than the rate of freezing, since all measurements shown were made at the same time. These results differ from some other published information. The fluorescence of dried eggs, prepared from liquid egg frozen at different rates, increased with increase in freezing time (5); but freezing and defrosting of extracts containing these fluorescing substances caused a reduction in fluorescence (3). Prolonged storage of frozen egg caused an increase in fluorescing substances (4).

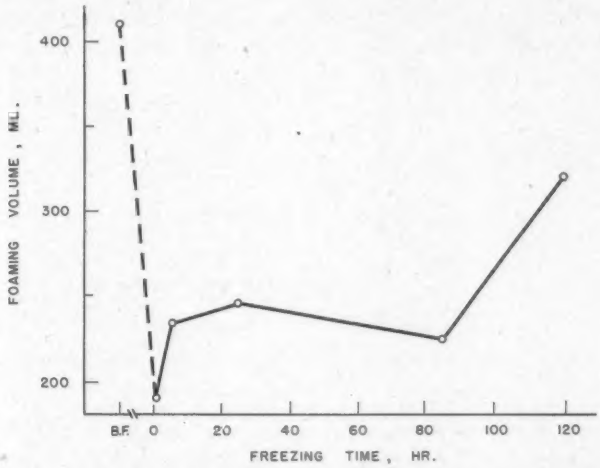

FIG. 2. *Effect of freezing time of yolk on the foaming volume of defrosted yolk mixed with unfrozen white.*

In general, freezing time had little effect on the foaming volume of defrosted whole egg or egg white, but it did affect foaming in defrosted yolk. Unfrozen whole egg had a foaming volume of about 400 ml. Frozen whole egg had a foaming volume of about 375 ml., regardless of the freezing time, while the foaming volume for mixtures of frozen white and unfrozen yolk was about 390 ml. regardless of the freezing time of the white. Fig. 2 shows that freezing yolk in about 100 hr. gave a product which, when mixed with an amount of unfrozen white to give whole egg liquid of correct proportions, had a foaming volume of about 300 ml., while yolk frozen in 10 min. had a foaming volume of only about 200 ml.

The Effect of Added Salt and Sugar on Frozen Yolk

Some explanations have been given for the effectiveness of sodium chloride and sucrose in reducing gelation in frozen yolk (1, 9). Since these substances are used commercially for this purpose (10), it was of interest to see if their

use also affected baking quality of yolk as reflected by foaming volume measurements. Therefore, 2, 4, and 8% of these compounds were added to yolk before freezing, and the samples were examined immediately after defrosting.

Fig. 3 shows that 2% sodium chloride had a marked effect in retaining the foaming volume of frozen yolk, and that increasing the amount of salt had

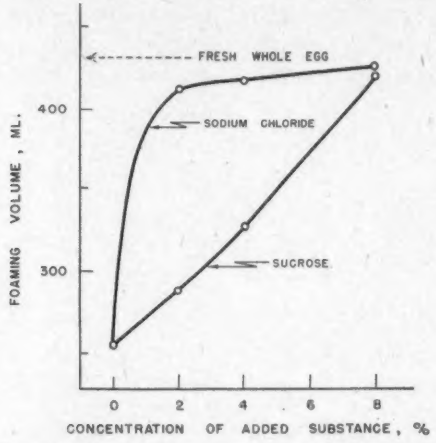

FIG. 3. *Effect of added sodium chloride and sucrose on the foaming volume of defrosted yolk and unfrozen white.*

only a slight additional effect. Increasing the amount of sucrose up to 8% had a progressively greater effect in retaining foaming volume: 8% sucrose gave a product that was about equal to fresh egg.

Effect of Storage Time on Quality

An earlier study in these laboratories indicated a decrease in the baking quality of freshly frozen whole egg (4). Therefore, it was of interest to re-

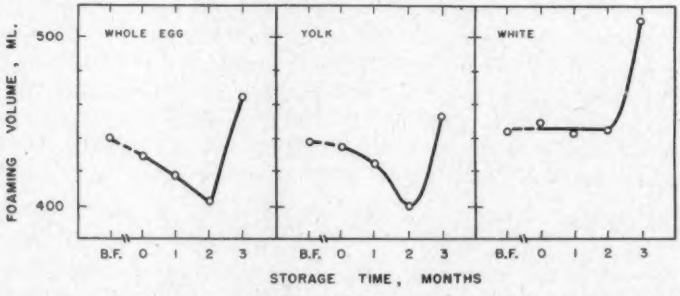

FIG. 4. *Changes in the foaming volume of stored frozen egg products: defrosted yolk mixed with unfrozen white, and defrosted white mixed with unfrozen yolk.*

examine the effect of storage up to about three months at − 10° F. on the quality of yolk, white, and whole egg.

Freezing and time of frozen storage effected measurable pH changes, in white and in whole egg, but pH could not be measured in defrosted yolk because of its high viscosity. Egg white had a pH of 9.0 before freezing, which increased to 9.1 after freezing and then gradually decreased to 8.9 at the end of three months' storage. Whole egg had a pH of 7.5 before freezing, which became 7.6 after freezing and then gradually increased to 7.8 after three months' storage. These pH changes in frozen whole egg were similar to those observed previously (4).

Fig. 4 shows that both whole egg and yolk decreased in foaming volume during freezing and the first two months of frozen storage, and then increased

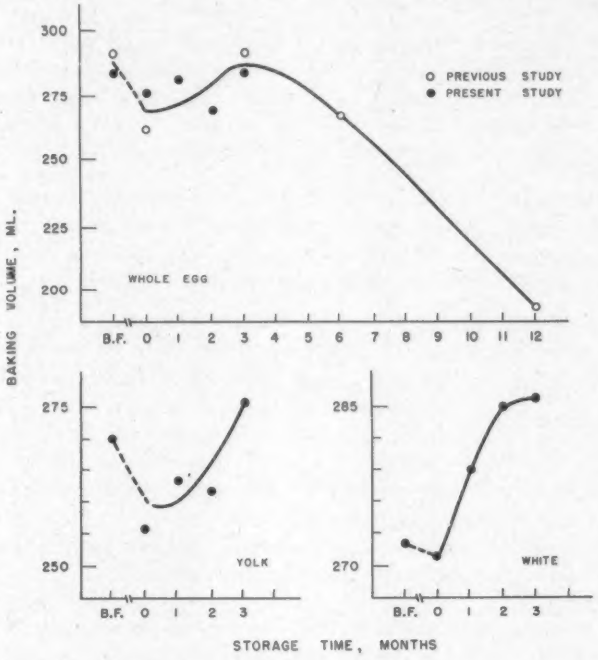

FIG. 5. *Changes in the baking volume of sponge cakes made from frozen egg products: defrosted yolk mixed with unfrozen white, and defrosted white mixed with unfrozen yolk.*

in foaming volume. The foaming volume of egg white remained constant during the first two months of storage, and increased during the third month. Earlier work showed that 12 months' frozen storage appreciably reduced the foaming volume of frozen whole egg (4).

Fig. 5 shows the reduction in baking quality resulting from freezing yolk or whole egg and the subsequent increase in quality after about three months'

storage. The baking quality of egg white appeared to be unchanged by freezing but to increase during the first three months' storage. In general, foaming volume and baking volume show similar changes during frozen storage and the results presented here support previous observations on stored, frozen whole egg (4).

Effect of Freezing and Thawing Time on Quality

During the preceding phase of this study, there was some evidence that thawing time might also have some effect on quality. Therefore, a more comprehensive study was made to examine the effects of freezing time (0.2, 4, 16, and 39 hr.), thawing time (0.03, 4, 24, and 48 hr.), and storage time (0, 1, 2, 4, and 8 months) at 0° F. on viscosity and baking volume of yolk and whole egg.

Just as this study commenced, the oven used in previous baking studies broke down. With the temporary equipment used, pending receipt of a new oven, the cakes were about 30 ml. smaller than usual. Therefore, while the results for this portion of the work are comparable within themselves, they cannot be readily compared with those of previous work.

The changes in viscosity and baking volume were assessed by an analysis of variance. Each of the factors under study had a significant effect on the viscosity of defrosted yolk and whole egg, but only thawing time and storage time had a significant effect on baking quality.

Fig. 6 shows the similarity in effect of these factors on the viscosity of both yolk and whole egg, except that yolk was much more viscous than whole egg. In general, increases in freezing time from 0.2 to 39 hr. caused progressive increases in viscosity; increases in defrosting time from 0.03 to 24 hr. caused increases in viscosity, but increases in thawing time from 24 to 48 hr. caused no further increase in viscosity. Storage time caused no increase in viscosity if the product was frozen or defrosted in four hours or less, but increasing the storage time increased the viscosity in product which had been frozen or defrosted in longer times. Measurements elsewhere had indicated maximum viscosity in defrosted whole egg after two to four months' storage (9); the present results showed a progressive increase in viscosity of slowly frozen or defrosted egg throughout an eight month storage period at 0° F.

In general, while viscosity was not related to the baking volume of defrosted yolk or whole egg, material of low viscosity was more easily prepared for baking. Frozen yolk was much more viscous than frozen whole egg, and usually gave cakes about 20 ml. smaller. However, the difference in cake volume was attributable to factors other than the freezing operation, since cakes made from yolks that had been mechanically mixed, but not frozen, and added back to white also gave cakes about 20 ml. smaller than those from whole egg (Fig. 5).

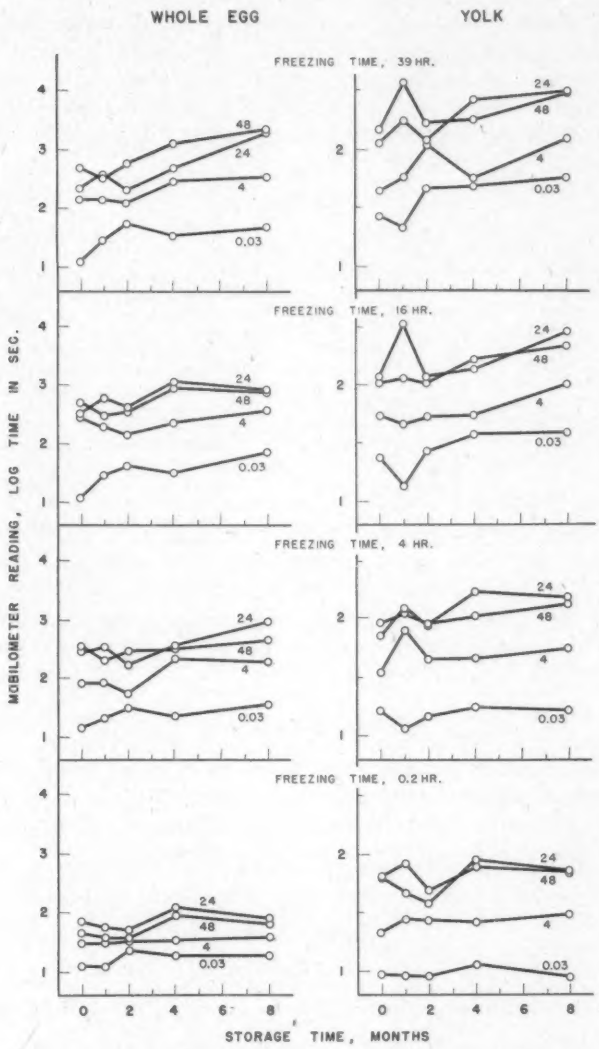

FIG. 6. *Effect of freezing time, thawing time (small labelled figures give the thawing time in hours), and storage time on the viscosity of defrosted yolk and whole egg.*

Fig. 7 shows that product thawed in four hours gave cakes with greater volume than product thawed in shorter or longer thawing times. While these differences were statistically significant, the increase in baking volume was only about 3%, which may not be of practical value in commercial processing.

Storage time had effects on the baking volume of cakes made from defrosted whole egg similar to those shown in Fig. 5. The baking volume of defrosted yolk was decreased by freezing and increased after four months' storage in a manner similar to that shown in Fig. 4; but in addition, there was evidence that the baking volume of defrosted yolk decreased between four and eight months' storage.

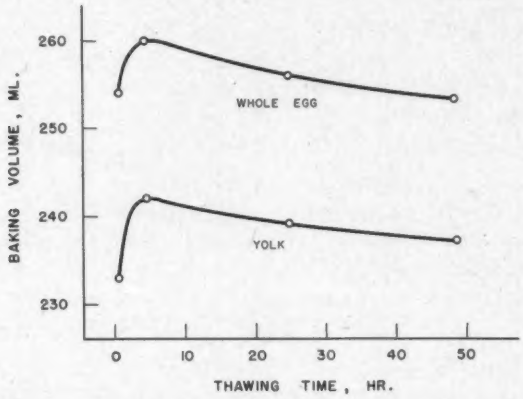

FIG. 7. *Effect of thawing time on the baking volume of sponge cakes made from defrosted whole egg, and from defrosted yolk mixed with unfrozen white. Values averaged over all freezing times and storage times.*

Acknowledgments

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THE THIAMINE AND RIBOFLAVIN CONTENT OF MANITOBA GROWN WHEAT, OATS, AND BARLEY OF THE 1946 CROP[1]

ALLEN D. ROBINSON,[2] LANGTRY E. LYND,[3] AND BARBARA J. MILES[3]

Abstract

Some 200 samples of pure varieties of barley, oats, and wheat grown in Manitoba in 1946 were assayed for thiamine and riboflavin. Expressed as micrograms per gram the averages and ranges for thiamine were: barley 4.06 (3.3 to 4.9), oats 5.99 (4.4 to 7.9), wheat 4.28 (3.5 to 5.7); for riboflavin: barley 1.28 (0.9 to 1.9), oats 1.25 (0.8 to 1.7), wheat 1.12 (0.8 to 1.4). A varietal effect on thiamine content was noted. Plush barley contains more than OAC 21, Exeter oats more than either Ajax or Vanguard, and Carlton wheat more than Regent, which in turn has a higher content than Thatcher. No varietal effects on riboflavin contents were found in any of the cereals. Neither thiamine nor riboflavin content of the cereals was determined by the soil zone in which they were grown. Significant positive correlations were found between protein and thiamine in oats and barley, protein and riboflavin in wheat, and ash and riboflavin in barley. A significant negative correlation between ash and thiamine in oats was observed.

Recently McElroy, Kastelic, and McCalla (9) have reported on the thiamine and riboflavin contents of wheat, oats, and barley grown in Alberta and the effect of type of soil on the amount of vitamin in each of these grains. This is a report of a similar investigation carried out with grains grown in Manitoba in 1946. As in the study to which reference has been made, the correlation between vitamin contents and those of other constituents was studied.

A large number of values have been reported for the thiamine contents of wheats. Some have been reported for other cereals as well. There are fewer data for riboflavin. Some of the published results are summarized in Table I. Several of these were reported originally in terms other than micrograms per gram and have been calculated by us to this basis.

The factors responsible for the varying amounts of vitamins in cereal grains have not been very well defined. A varietal effect in wheat seems to be well established. Jackson and Whiteside (7) and Whiteside and Jackson (12) found significant differences to exist between the thiamine contents of different Canadian hard red spring wheat varieties. Regent, Renown, and Reward are usually higher in thiamine than Red Bobs, Thatcher, Marquis, and Garnet. Andrews *et al.* (3) found differences in the riboflavin contents of different varieties of wheat. They listed the varieties tested, in the order of decreasing riboflavin contents, as Marquis, Pilot, Thatcher, Ceres, Renown, Rival.

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[2] *Associate Professor of Chemistry.*

[3] *Research Assistant.*

TABLE I

THIAMINE AND RIBOFLAVIN CONTENTS OF BARLEY, OATS, AND WHEAT, MICROGRAMS PER GRAM

Reference	Thiamine		Riboflavin	
	Range	Average	Range	Average
Barley				
Andrews, Boyd, and Terry (3)	—	—	1.05–1.50	1.21
Davis, Laufer, and Saletan (4)	4.91–6.52	—	0.78–1.14	—
Hochberg, Melnick, and Oser (6)	—	3.50	—	—
McElroy, Kastelic, and McCalla (9)	—	4.60	—	1.25
Nordgren and Andrews (10)	5.68–7.33	6.49	—	—
Schultz, Atkin, and Frey (11)	3.8–9.2	6.2	—	—
Oats				
Andrews *et al.* (3)	—	—	1.10–1.45	1.30
McElroy *et al.* (9)	—	5.58	—	1.27
Nordgren and Andrews (10)	8.10–10.78	9.24	—	—
Schultz *et al.* (11)	4.8–10.3	7.2	—	—
Wheat				
Andrews *et al.* (3)	—	—	1.06–1.32	—
Davis *et al.* (4)	—	—	0.71–1.12	—
Johannson and Rich (8)				
Literature review	1.62–10.2	—	—	—
Original data	2.2–8.0	3.93	—	—
McElroy *et al.* (9)	—	4.40	—	1.34
Whitney, Herren, and Westerman (13)	—	—	1.00–1.69	—

Nordgren and Andrews (10) and Whiteside and Jackson (12) found environment to be a significant factor in determining the thiamine content of wheat. Wheat was grown in different localities for several seasons. Certain localities produced wheat with a higher thiamine content than others, even though the amounts varied from season to season. The features of environment that might be causing this effect were not investigated. Johannson and Rich (8), working with commercial samples of wheat, did not observe any relation between soil type and thiamine content of the grain. McElroy *et al.* (9) found the thiamine contents of wheat, oats, and barley grown on brown soils to be significantly higher than those grown on gray ones. The mean riboflavin contents of samples of wheat, barley, and oats grown on gray soils were slightly lower than those of samples grown on black or brown ones. Andrews *et al.* (3) found that the riboflavin content of wheat is not significantly affected by environment.

Some studies have been made to determine whether vitamin content is related to the content of any other constituent. Nordgren and Andrews (10) found a significant correlation between ash and thiamine in American-grown spring wheats, but not in winter or Western Canadian spring wheats. They did not find a significant correlation between protein and thiamine contents. McElroy *et al.* (9) found a positive correlation between protein and thiamine content for wheat and oats, but not for barley. No significant correlation

between protein and riboflavin was found in any of the three cereals. Johannson and Rich (8) failed to find any relation between amounts of thiamine in wheat and either protein or ash content. Whiteside and Jackson (12) after studying the distribution of thiamine in the wheat kernel conclude that the physical features of the kernel that are associated with high protein would also be associated with high thiamine. No relation has been established however which would permit the prediction of vitamin contents from those of any other constituent.

Further studies of vitamin contents of grains should yield results of interest. The effect of soil deserves more extended investigation. While some attempts have been made to determine if there is any relation between vitamin contents and the contents of other constituents, different investigators have reported different findings. The coarse grains have not been studied to the degree their importance warrants. The investigation reported herein details a study of the thiamine and riboflavin contents of barley, oat, and wheat varieties grown commonly in Manitoba. The samples were from the 1946 crop. They were assayed for protein, ash, thiamine, and riboflavin. An attempt was made to correlate these results with each other and with variety and soil zone.

Experimental

More than 200 samples of pure varieties of barley, oats, and wheat were collected. These were grown in several different parts of the province. The soil type was determined for each of these locations.

Moisture was determined on each sample by the 130° C. oven method, ash by direct ignition in the muffle furnace, and protein by the Kjeldahl procedure. Thiamine was determined by the Hennessy (5) method using an external standard and calculating results on the basis of a 94% recovery. Riboflavin was determined by the method of Andrews (1, 2) with the following modifications: an external standard was used instead of an internal one, and a solution of sodium hydrosulphite and sodium bicarbonate replaced solid sodium hydrosulphite. The results of analyses were calculated to a 13.5% moisture level.

Results and Discussion

The thiamine and riboflavin results for barley, oats, and wheat, grouped according to variety and soil type, are found in Tables II, III, and IV, respectively.

Barley

An examination of the data for barley reported in Table II reveals several interesting features. The small number of samples of Garton, together with the large standard deviation for this variety, and the large standard deviation for Sanalta make any conclusions doubtful regarding these varieties, since their averages differ from those for OAC 21 and Plush by only small amounts.

TABLE II

THIAMINE AND RIBOFLAVIN CONTENT OF BARLEY GROUPED ACCORDING TO VARIETY AND SOIL ZONE

Variety	Garton			OAC 21			Plush			Sanalta		
Soil zone	No. of samples	Vitamin, μgm./gm.		No. of samples	Vitamin, μgm./gm.		No. of samples	Vitamin, μgm./gm.		No. of samples	Vitamin, μgm./gm.	
		Mean	S. d.		Mean	S. d.		Mean	S. d.		Mean	S. d.
Thiamine												
Rendzina	–	–	–	2	3.95	0.05	2	4.30	0.30	–	–	–
Degraded rendzina	–	–	–	–	–	–	1	4.5	–	–	–	–
Black earth	2	4.00	0.40	3	3.80	0.16	5	4.14	0.08	4	4.23	0.44
Black earth–rendzina	–	–	–	–	–	–	1	4.5	–	–	–	–
Dark brown steppe–black earth transition	–	–	–	–	–	–	2	4.30	0.50	3	4.17	0.20
Northern black	–	–	–	3	3.77	0.20	5	4.03	0.22	3	4.07	0.18
Northern black–gray black	–	–	–	–	–	–	–	–	–	1	3.3	–
Gray black	1	5.1	–	1	4.2	–	2	4.00	0.10	–	–	–
Gray wooded–gray black	–	–	–	–	–	–	1	4.2	–	1	2.9	–
Gray wooded	1	4.2	–	1	3.6	–	1	4.6	–	–	–	–
All soil zones	4	4.33	0.54	10	3.84	0.21	20	4.19	0.28	12	3.98	0.50
Riboflavin												
Rendzina	–	–	–	2	1.40	0.30	2	1.40	0.50	–	–	–
Degraded rendzina	–	–	–	–	–	–	1	1.4	–	–	–	–
Black earth	2	1.40	0.10	3	1.13	0.10	5	1.26	0.10	4	1.28	0.13
Black earth–rendzina	–	–	–	–	–	–	1	1.2	–	–	–	–
Dark brown steppe–black earth transition	–	–	–	–	–	–	2	1.35	0.05	3	1.33	0.17
Northern black	–	–	–	3	1.40	0.14	5	1.14	0.19	3	1.30	0.08
Northern black–gray black	–	–	–	–	–	–	–	–	–	1	1.4	–
Gray black	1	1.4	–	1	1.3	–	2	1.20	0.10	–	–	–
Gray wooded–gray black	–	–	–	–	–	–	1	0.9	–	1	1.3	–
Gray wooded	1	1.6	–	1	1.6	–	1	1.5	–	–	–	–
All soil zones	4	1.45	0.11	10	1.33	0.22	20	1.25	0.23	12	1.31	0.13

Plush contains more thiamine than OAC 21: this is true not only for the grand averages for these varieties, but for the averages for each soil zone—except gray black—on which the two varieties were grown.

There does not seem to be any effect of soil zone on the thiamine content of barley. Where there does appear to be some order, as an apparent decreasing one of rendzina, black earth, and northern black for OAC 21, Plush, and—for the last two zones named—Sanalta, the standard deviation for each group is usually as large as the difference between the averages. This was confirmed by an analysis of variance. Since the samples were not evenly distributed between varieties and the soil zones it was not possible to use all the data. But an analysis was made for OAC 21 and Plush for the five soil zones in which both were grown, the extra values being eliminated by using

TABLE III

THIAMINE AND RIBOFLAVIN CONTENT OF OATS GROUPED ACCORDING TO VARIETY AND SOIL ZONE

Variety / Soil Zone	Ajax			Exeter			Vanguard		
	No. of samples	Vitamin, μgm./gm.		No. of samples	Vitamin, μgm./gm.		No. of samples	Vitamin, μgm./gm.	
		Mean	S.d.		Mean	S.d.		Mean	S.d.
Thiamine									
Rendzina	3	5.10	0.45	–	–	–	3	5.83	0.81
Degraded rendzina	1	5.8	–	–	–	–	–	–	–
Black earth	10	5.87	0.36	5	6.80	0.93	7	5.40	0.67
Dark brown steppe–black earth transition	2	6.45	0.45	–	–	–	–	–	–
Northern black	4	6.38	0.40	2	7.75	0.15	4	5.60	1.26
Northern black–gray black	–	–	–	–	–	–	1	6.6	–
Gray black	–	–	–	2	6.05	0.35	1	4.9	–
Gray wooded–gray black	–	–	–	–	–	–	1	7.0	–
Gray wooded	2	5.65	0.25	–	–	–	–	–	–
All soil zones	22	5.89	0.55	9	6.84	0.92	17	5.66	0.94
Riboflavin									
Rendzina	3	1.20	0.08	–	–	–	3	1.20	0.08
Degraded rendzina	1	1.3	–	–	–	–	–	–	–
Black earth	10	1.15	0.19	5	1.24	0.21	7	1.21	0.10
Dark brown steppe–black earth transition	2	1.40	0.10	–	–	–	–	–	–
Northern black	4	1.13	0.28	2	1.30	0.00	4	1.30	0.24
Northern black–gray black	–	–	–	–	–	–	1	1.7	–
Gray black	–	–	–	2	1.25	0.05	1	1.2	–
Gray wooded–gray black	–	–	–	–	–	–	1	1.5	–
Gray wooded	2	1.60	0.20	–	–	–	–	–	–
All soil zones	22	1.22	0.24	9	1.26	0.15	17	1.28	0.31

tables of random numbers. In no case was the F value for soil zones as large as the 5% point. The difference between the thiamine contents of Plush and OAC 21 was, however, found to be significant. This confirms the observations made in the preceding paragraph.

The data for riboflavin in barley appear in the lower half of Table II. The spread between the lowest variety, Plush, and the highest, Garton, is only 0.2 μgm. per gm. while standard deviations range from 0.11 for Garton to 0.23 for Plush. No one soil zone produces consistently higher or lower

values for all varieties. Most groups differ from the average for the variety by less than the standard deviation for the group. There is then no obvious effect of either soil zone or variety on the riboflavin content of barley. This was confirmed by an analysis of variance for the same varieties and soil zones as were used in the analysis of the thiamine data. There was no significant difference between either soil zones or the varieties Plush and OAC 21. In each case the F value was less than that for the 5% point.

Oats

The thiamine contents of three varieties of oats are recorded in the upper half of Table III. Exeter shows the highest values, on the average and for each group according to soil zone. It would appear that it is the best as a source of thiamine even though the standard deviation of 0.92 is rather large. Ajax and Vanguard are much the same in thiamine content. An analysis of

TABLE IV

THIAMINE AND RIBOFLAVIN CONTENT OF WHEAT GROUPED ACCORDING TO VARIETY AND SOIL ZONE

Variety	Carlton			Regent			Renown			Thatcher		
Soil zone	No. of samples	Vitamin, µgm./gm.		No. of samples	Vitamin, µgm./gm.		No. of samples	Vitamin, µgm./gm.		No. of samples	Vitamin, µgm./gm.	
		Mean	S. d.		Mean	S. d.		Mean	S. d.		Mean	S. d.
Thiamine												
Rendzina	–	–	–	1	4.8	–	–	–	–	4	4.03	0.33
Degraded rendzina	–	–	–	1	5.0	–	1	4.2	–	5	3.70	0.18
Black earth	10	5.03	0.42	30	4.27	0.34	4	4.13	0.11	7	4.06	0.28
Black earth–rendzina	–	–	–	1	4.1	–	–	–	–	–	–	–
Dark brown steppe–black earth transition	1	4.6	–	3	4.38	0.23	–	–	–	2	3.9	0.00
Northern black	–	–	–	13	4.33	0.31	–	–	–	6	3.95	0.15
Northern black–gray black	–	–	–	1	4.9	–	–	–	–	–	–	–
Gray black	–	–	–	5	4.36	0.47	–	–	–	7	4.10	0.17
Gray wooded	–	–	–	2	4.15	0.05	–	–	–	1	3.9	–
All soil zones	11	4.99	0.42	57	4.33	0.34	5	4.14	0.10	32	3.97	0.26
Riboflavin												
Rendzina	–	–	–	1	1.0	–	–	–	–	4	1.08	0.08
Degraded rendzina	–	–	–	1	1.4	–	1	1.2	–	5	1.18	0.04
Black earth	10	1.05	0.17	30	1.12	0.14	4	1.05	0.15	7	1.11	0.16
Black earth–rendzina	–	–	–	1	1.1	–	–	–	–	–	–	–
Dark brown steppe–black earth transition	1	1.2	–	3	1.10	0.10	–	–	–	2	1.15	0.15
Northern black	–	–	–	13	1.18	0.09	–	–	–	6	1.15	0.11
Northern black–gray black	–	–	–	1	1.3	–	–	–	–	–	–	–
Gray black	–	–	–	5	1.18	0.16	–	–	–	7	1.04	0.12
Gray wooded	–	–	–	2	1.10	0.10	–	–	–	1	1.0	–
All soil zones	11	1.06	0.17	57	1.14	0.14	5	1.08	0.15	32	1.11	0.12

variance for these two varieties for rendzina, black earth, and northern black soil zones showed no significant difference of thiamine content between varieties or soil zones.

The content of riboflavin in oats is more uniform than in barley. The averages for varieties differ by only 0.06 μgm. per gm., which is much less than the standard deviation for any one variety. Analysis of variance indicated that differences between varieties, as well as between soil zones, were not significant.

Wheat

Four wheat varieties were assayed for thiamine, as is indicated by the data in the upper half of Table IV. Decreasing amounts of this vitamin as shown by variety averages occur in Carlton, Regent, Renown, and Thatcher. The first of these was grown on only two soil zones, but its value for each of these was higher than for any of the other three varieties grown in the same zone. Since its over-all average is 0.66 μgm. per gm. higher than for the second variety and its standard deviation is 0.42 it would seem to be easily the best of the four. Only five samples of Renown were collected, and from two soil zones, so little can be concluded about it. That the difference between Regent and Thatcher is significant is shown by an analysis of variance for these two varieties grown in seven soil zones. This difference has already been mentioned by Jackson and Whiteside (7) and Whiteside and Jackson (12). At the same time the analysis of variance did not reveal any significant differences between soil zones.

That the riboflavin contents of these four varieties are much the same is shown by a comparison of the averages reported in the lower half of Table IV. The difference of 0.08 between the lowest and highest riboflavin contents is meaningless. This is not in accord with the findings of Andrews *et al.* (3), who reported Thatcher wheat to contain more riboflavin than Renown. An examination of soil zone averages reveals no marked differences for the various zones. The lowest average for a group containing at least two samples is 1.05 μgm. per gm., the highest 1.18. Most standard deviations approach or exceed the difference between these two. Again there is no uniformity in order of riboflavin content by soil zone for the different varieties. These general conclusions were verified by an analysis of variance for riboflavin content of Regent and Thatcher wheats grown on seven soil zones.

Correlation coefficients for thiamine with riboflavin and for each of the vitamins with protein and ash were calculated for each of the three cereals. These values are reported in Table V. There are significant positive correlations between protein and thiamine in oats and barley and between protein and riboflavin in wheat. There is no correlation between protein and thiamine in wheat or between protein and riboflavin in oats and barley. A significant positive correlation is found between ash and riboflavin in barley and a significant negative one between ash and thiamine in oats.

TABLE V

CORRELATION COEFFICIENTS FOR THIAMINE AND RIBOFLAVIN WITH PROTEIN AND ASH

Cereal	Barley	Oats	Wheat
Number of samples	48	54	102
Protein–thiamine	.5042**	.7432**	.0331
Protein–riboflavin	.0949	.1393	.2514**
Ash–thiamine	—.0993	—.3016*	—.0038
Ash–riboflavin	.3641*	.0886	.1572
Thiamine–riboflavin	.0718	.1580	.0663

**Within 5% level of significance.*
***Within 1% level of significance.*

The lack of a significant correlation between thiamine and either protein or ash in wheat is in harmony with the findings of Johannson and Rich (8), though contrary to those of McElroy *et al.* (9), who found one for protein and thiamine. These authors report one for protein and thiamine in oats, which is confirmed by our results. Their results did not show one for protein and thiamine in barley, whereas the one obtained in this investigation is within the 1% level of significance. The lack of a significant correlation for ash and thiamine in wheat confirms the earlier report of Nordgren and Andrews (10) who found none for winter wheats or Western Canadian spring wheats, though they did for American-grown spring wheats. Our not obtaining a correlation between riboflavin and protein in barley and oats confirms the results of McElroy and his coworkers, but the one between riboflavin and protein in wheat does not.

The significant correlations are of interest and may indicate a causal relation. The values are too small to permit the prediction of vitamin contents from ash or protein ones.

Acknowledgments

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A SIMPLE ELECTRICAL METER FOR ESTIMATING THE MOISTURE CONTENT OF GRAIN[1]

H. E. RASMUSSEN[2] AND J. A. ANDERSON[3]

Abstract

A simple electrical meter has been devised for estimating the moisture content of grain. It accommodates a 190 gm. sample which forms the dielectric of a condenser in the plate tuning circuit of a triode crystal oscillator. An increase in the dielectric constant due to moisture in the sample is compensated for by removing capacity from a variable condenser attached to the dial of the instrument. A piezoelectric plate determines the frequency at which the triode section of the tube will oscillate, and this state is indicated by a change in the shadow angle of the indicator section of the same tube. The meter has been calibrated with 159 samples of Canadian hard red spring wheat; the standard error of estimate was found to be 0.36 over the range from 10 to 17% moisture.

A number of electrical meters for estimating the moisture content of grain by measuring electrical properties are now commercially available. In most of these, the dielectric constant of the grain is determined by frequency deviation or phase shift methods which involve relatively complex circuits and the use of accurate indicating instruments. The meters are therefore expensive. A meter with a simpler electrical circuit, which it should be possible to manufacture and market more cheaply, was devised by one of us (H.E.R.) in 1945. A similar circuit has since been described by Fischer (1). The G.R.L. meter (christened with the initials of this Laboratory) is described in the following three sections dealing with design, circuit, and operation.

General Design

A photograph of the instrument is shown in Fig. 1. All components are attached to an etched metal panel supported on an oak case which houses the measuring circuit and power supply. The rectangular tube at the back of the photograph (inside dimensions, 10 by 5.5 by 0.75 in.) extends about equally above and below the panel. It has spring-loaded horizontal gates in the center and at the bottom, and thus provides a loading hopper and a measuring cell. A white push knob for opening the gate that dumps grain into the cell is shown at the left of the hopper; a corresponding knob on the right controls the gate that empties the grain from the cell into the drawer in the end of the oak case. Small black knobs at front and back are the power switch and fuse mount. The main dial of the instrument is shown at the front. Between this and the hopper there is a shield which protects the top of an electronic tube that indicates, by a change in the shadow angle,

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Paper No. 97 of the Grain Research Laboratory, Board of Grain Commissioners for Canada, Winnipeg, Manitoba, and No. 269 of the Associate Committee on Grain Research.
[2] *Senior Technician.*
[3] *Chief Chemist.*

when the dial has been correctly adjusted in making a reading. Other mechanical details are not described because they are relatively unimportant and will doubtless be changed if the meter is redesigned for factory production.

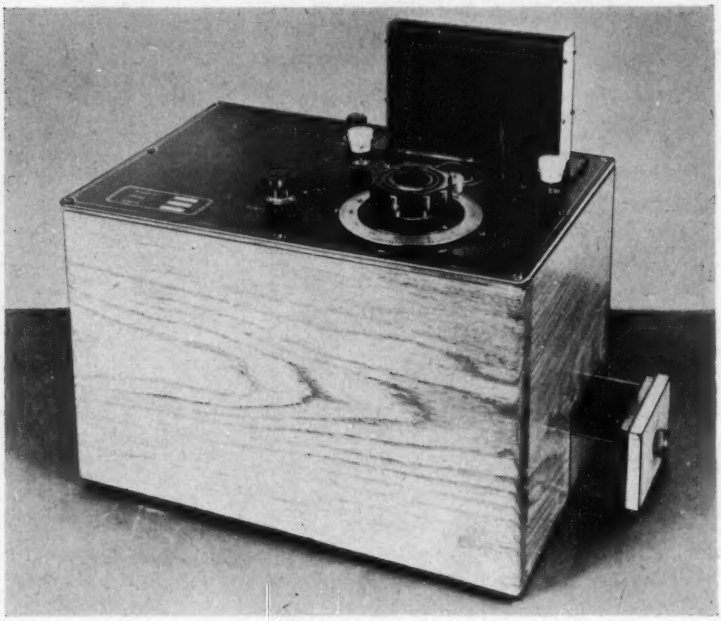

FIG. 1. *Photograph of G.R.L. moisture meter.*

Electrical Circuit

The circuit is shown in Fig. 2. A 6E5 electron ray indicator and triode tube T has the plate circuit tuned to the frequency (7.3 Mc.) of a piezoelectric plate by a resonant circuit consisting of an inductance L and three condensers, C_1, C_2, and C_3, in parallel.

Variable condenser C_1 (30 $\mu\mu$f.) can be set with a screwdriver and is used merely to compensate for unpredictable interelectrode and distributed capacitances of the circuit components. Variable condenser C_2 (15 $\mu\mu$f.) has attached to it the dial of the instrument, and its capacitance can thus be varied to tune the plate circuit. Each dial division represents 0.144 $\mu\mu$f. capacitance. The condenser C_3 is a dielectric cell in which the grain is placed. It consists of two aluminum plates, 8.9 cm. by 12.0 cm., spaced 1.9 cm. apart, attached to the insides of the bakelite walls of the rectangular tube previously described. Capacitance at the terminals of the cell, when empty, is 17.0 $\mu\mu$f.

When grain is placed in the cell, the capacitance is increased by an amount which is a function of the moisture content of the grain. The dial is then turned to remove capacitance from C_2 until the product $L\ (C_1 + C_2 + C_3)$ attains the value at which oscillation begins. The decrease in plate current through the resistor R (100,000 ohm) then causes an abrupt increase in the shadow angle of the indicator section of tube T. When this change is observed, the position of the dial is read on an arbitrary scale.

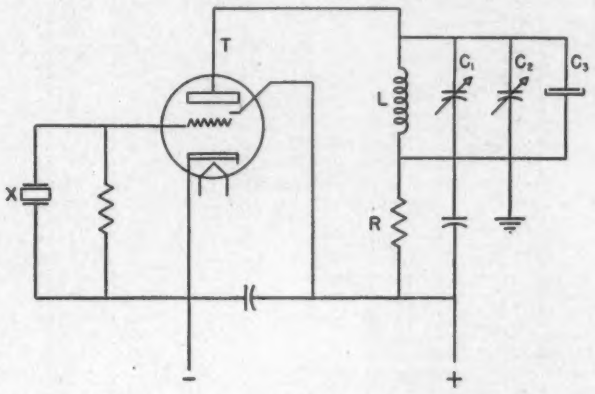

FIG. 2. *Circuit for G.R.L. moisture meter.*

Owing to the very high Q of the oscillator grid circuit, the value of plate tuning capacitance at which the crystal begins to oscillate is critical, especially when approached from the capacitive side. Once oscillations have started, a larger change in plate tuning capacity is necessary before the circuit drops out of oscillation. Accordingly, the point of balance must be approached slowly, so that the meter reading will represent the beginning of oscillations.

Power is obtained from a full wave rectifier, a resistance capacity filter, and a pair of voltage regulating tubes. The instrument is designed for 115 v. a-c., but variations of $\pm$ 10 v. do not affect its operation. Alternatively, power could be readily supplied by batteries or Vibropack.

Operation

Before making a reading, the power must be turned on and the instrument allowed to warm up for five minutes. The dial is then turned anticlockwise against a mechanical stop. A 190 gm. sample of wheat, the temperature of which must be known, is poured into the hopper and roughly leveled. Sharp depression of the loading knob dumps this grain into the cell under conditions that ensure uniform packing. The dial is then turned clockwise until the shadow angle of the indicator tube opens. For the most accurate reading, the dial should then be turned back so that the estimated equilibrium point

can be approached more slowly. Dial readings are converted to percentage moisture by referring to a chart, and the converted reading is subsequently corrected for temperature.

The meter has been calibrated with 159 samples of hard red spring wheat taken from carlot shipments made during the 1947-48 crop year. Moisture determinations were made on duplicate subsamples by preliminary drying at room temperature, grinding, and drying overnight in a vacuum oven at

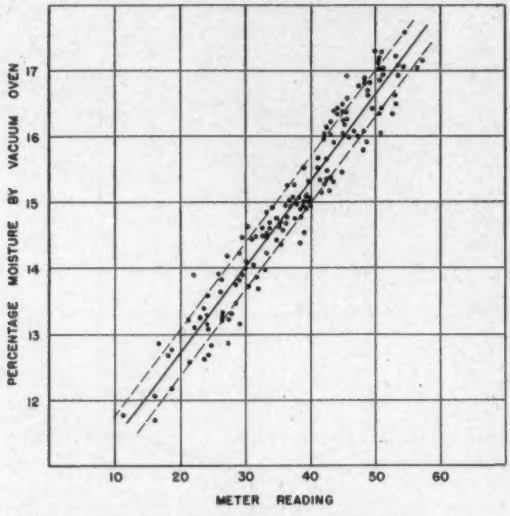

FIG. 3. *Scatter diagram showing relation between moisture contents of wheat determined by the vacuum oven method and by the G.R.L. moisture meter.*

100° C. Meter readings were made on duplicate subsamples in a room maintained at 72° ± 0.5° F. in which both meter and samples had been held for at least two days. Fig. 3 shows the resulting scatter diagram for the plot of vacuum oven moistures against meter readings. The regression equation is: vacuum oven moisture = 0.132 × meter reading + 10.06; the standard error of estimate is 0.36% moisture. A preliminary study of the effect of temperature indicates that the correction is 0.06% per 1° F.; this is added for temperatures above and subtracted for temperatures below 72° F.

This study comprised part of a larger investigation in which nine meters were compared; a paper on this work is in preparation for early publication. The G.R.L. meter ranked fourth in accuracy. Errors of estimates for the remaining eight meters were 0.23, 0.28, 0.35, 0.41, 0.45, 0.48, 0.49, and 0.58. The two most accurate instruments measure resistance; so that the G.R.L. meter, in spite of its simplicity, is essentially equal in performance to the best dielectric moisture meters tested in this laboratory.

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